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GB 2036595 A GB 1510486 A GB 1362742 A
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(54) Abstract Title
Separation using a coiled elastomeric membrane

(57) One or more tubular elastomer membranes 2 is enclosed within a coiled flexible shell 1 whose maximum coiled linear dimension is no more than one-tenth of its maximum uncoiled linear dimension, which may be eg 5m - 100m. The coil may have a diameter 30-50 times the shell internal diameter. The membrane(s) may bear longitudinal surface ridges (3, Fig 1). The assembly is useful in chemical, especially biological, separations in which the concentration of a component to be transferred across the membrane is small eg less than 2%. First and second fluids, located respectively inside the membrane tube and between the membrane and the shell, may be passed in co-current during the separation; the fluids may be two liquids or a liquid and a gas.

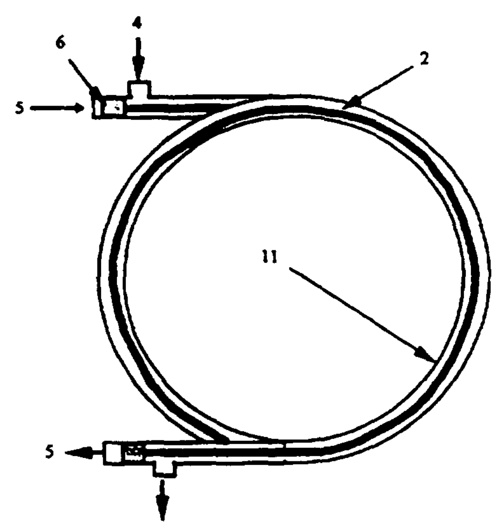

Figure 3

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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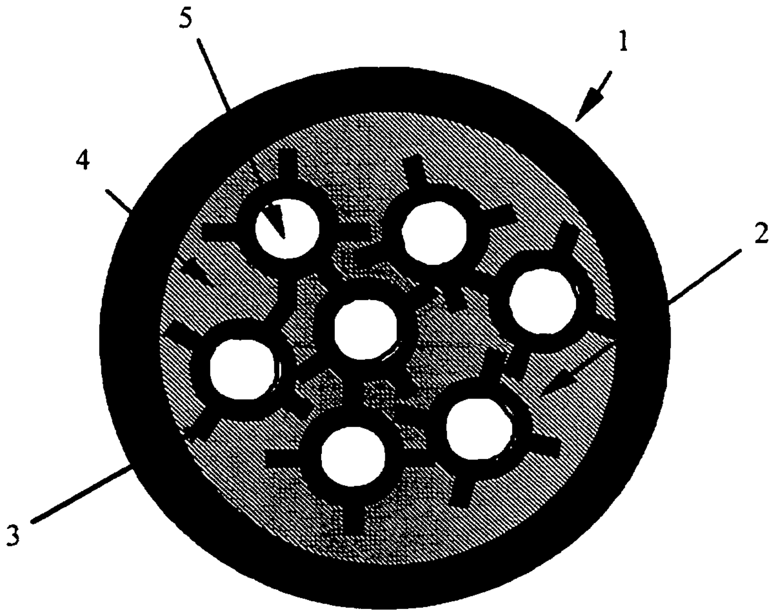

Figure 1

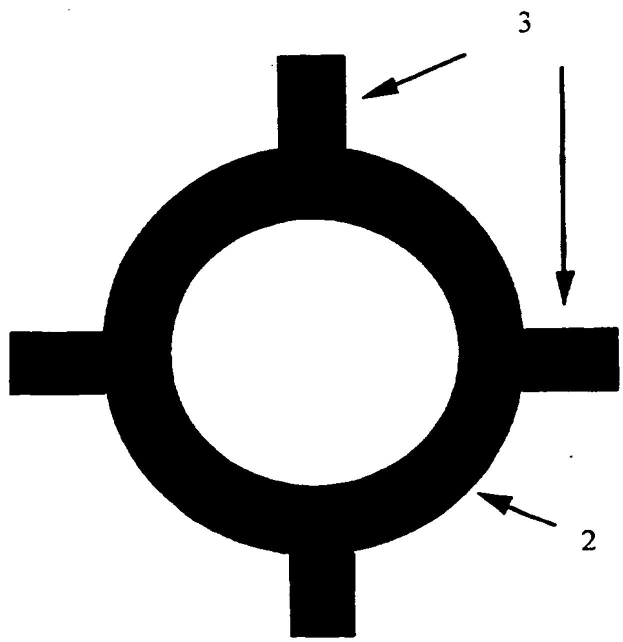

Figure 2

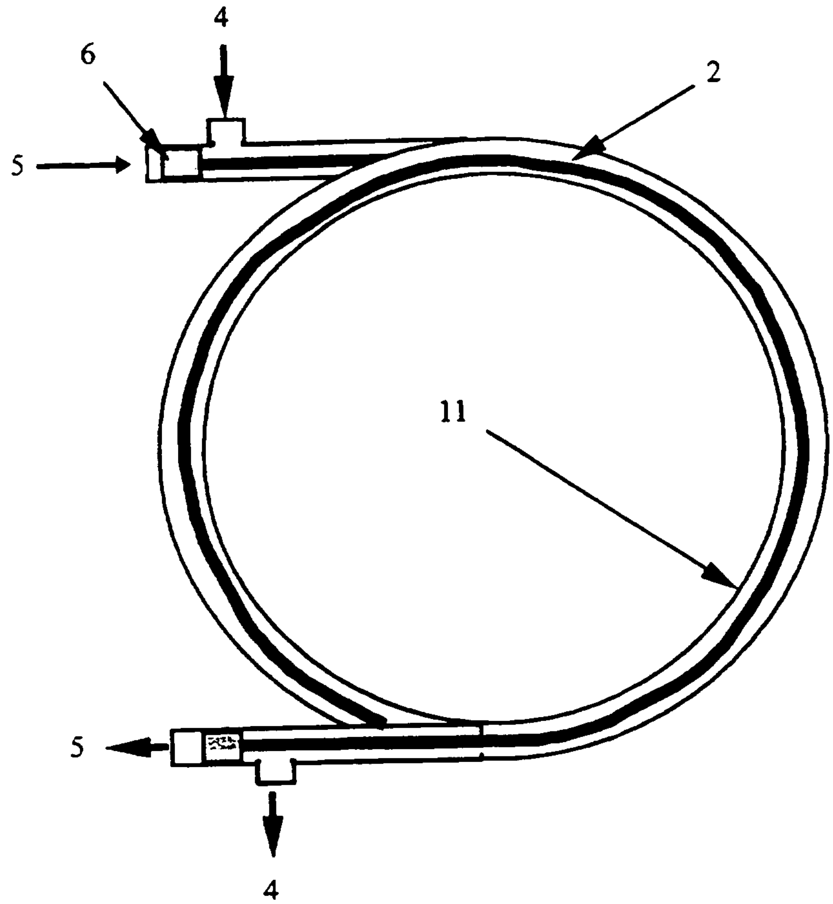

Figure 3

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Method

The present invention relates to a method for contacting two fluids and an apparatus useful in that method. Specifically, the present invention relates to a method for contacting liquid or gas streams for the purposes of allowing specific chemical species to selectively permeate across a non porous elastomeric membrane from one stream to another.

Methods for contacting two liquid streams in order to effect permeation of specific chemical species between the streams are generally well known. For example, in the field of aqueous waste treatment, US-A-4,988,443 discloses a method for contacting an aqueous waste stream containing organic toxicants with a nutrient-containing aqueous stream using a porous hollow fibre membrane. The pores of the membrane are filled with water immiscible solvent. The two streams do not mix but the organic toxicants may be transferred from the waste stream across the membrane to the nutrient stream. Micro-organisms growing associated with the outside of the hollow fibres utilise the nutrients and organic toxicants as growth substrates and proliferate.

SU-Al-1263654 discloses a treatment of wastewaters containing heavy metals. A microbial culture capable of producing hydrogen sulphide is contacted with one side of a membrane, while a wastewater containing heavy metals is contacted with the opposite side. Microbially produced hydrogen sulphide permeates across the membrane causing the metals in the wastewater to precipitate as insoluble sulphides.

In other systems which have been reported in the literature, chemical species present in a gaseous phase are reported to permeate across hollow fibre membranes and be absorbed, for example in Yang and Cussler, AlChE Journal, 1986 32 p1910 into liquids on the opposite side of the membrane.

Membrane based extraction systems have also been disclosed in connection with extraction of alcohol from beverages. For example see WO 87/02380.

In the field of biotransformations, methods are generally well known for contacting two liquid streams in order to effect permeation of specific chemical species between the streams.

EP-A-0120285 discloses a porous membrane system designed to effect catalysis of a reaction utilising a hydrophobic substrate by an enzyme present in a hydrophilic phase. Here, the porous membrane is used to separate two liquids, one an aqueous phase containing the enzyme and one an organic phase comprising the hydrophobic substrate. When the two phases make contact at the pore-membrane surface interface, the reaction proceeds.

EP-A-0112812 describes a system in which two liquid zones are separated by a semi-permeable membrane. In use, the membrane is permeable to predetermined reactant and product materials while being impermeable to catalytically active cell material that is essentially confluently packed in the second zone. The reactant material supplied to the first zone permeates the membrane and contacts the catalyst in the second zone, thereby forming product material. Product material permeates across the membrane and is removed from the first zone.

In the following description the term "tubular" means having a hollow body which defines an internal volume. The body may or may not have a circular cross-section. The body may or may not be continuous in any particular plane or direction.

In general, the prior art systems utilise modules which comprise a rigid shell which contains a bundle of porous hollow fibre membranes. The hollow fibre membranes may be composite membranes. Composite membranes comprise a porous support coated with a thin layer of a non porous polymer which effects the separation (see Wijmans et al., Environmental Progress, 1990 9 p262).

In a few cases, tubular elastomeric non porous homogeneous membranes, for example silicone rubber (cross-linked polydimethoxysiloxane) tubes, have been used. Elastomeric non prous homogeneous membranes provide separation by

allowing specific chemical species (for example, oxygen or hydrophobic organic molecules such as benzene, toluene, or their derivatives) to preferentially dissolve in the membrane and permeate across the membrane by diffusion under the influence of a chemical activity driving force.

US-A-5585004 discloses a system wherein a waste stream containing toxic organic compounds is fed into the inside of selectively permeable silicone rubber membrane tubes which are suspended in a bioreactor receptacle filled with a biologically active medium. The toxic organic compounds diffuse across the silicone rubber membrane and into the biologically active medium. In the biologically active medium the toxic organic compounds are degraded by the microbial culture.

Further examples of the use of tubular elastomeric membranes are oxygenation of microbial systems (Cote et al, Journal of Membrane Science 1989 47 p107), and pervaporation (Raghunath and Hwang, Journal of Membrane Science 1992 65 p 147).

Coiled membranes are known in the art for improving mass transfer and ease of construction of membrane systems. GB-A-1435985, GB-A-13628742, GB-A-1181934, WO-A-97/05946 and US-A-4,568,648 all disclose coiled tubular membranes. GB-A-1435985 and GB-A-1181934 describe devices for dialysis in which coiled dialysis membranes are contained within a shell which is a sealed circular box. GB-A-1362874 describes a process for producing polymeric reverse osmosis membranes by winding the tubular membranes around a spool. A module is later formed by sealing this coiled membrane inside a suitable circular box. The advantages of membranes which have high length to diameter ratios and so require less end fittings are cited by these inventors.

WO-A-97/05946 describes a system in which porous membranes are tightly coiled so as to produce Dean vortices. The coiled membranes are held in a conventional straight shell. US-A-4,568,648 discloses a coiled silicone rubber membrane tube for use in a deoxygenating device. The coiled membrane tube is held in a straight

cylinder.

The present invention aims to overcome the problems of the prior art.

According to a first aspect of the present invention there is provided an apparatus comprising an elastomeric tubular membrane and a shell, wherein the membrane is partially or completely enclosed by a shell, and wherein the shell is coiled such that the maximum linear dimension of the coiled shell is no greater than one tenth of the maximum linear dimension of the shell in an uncoiled configuration.

According to a second aspect of the present invention there is provided a method of transferring at least one substance across a membrane from a first fluid to a second fluid, wherein transfer of the substance from the first fluid to the second fluid occurs across the membrane; wherein the membrane is an elastomeric tubular membrane; wherein either the first fluid or the second fluid is held within the internal volume of the membrane and wherein the other of the first fluid or the second fluid is in contact with the external surface of the membrane;
wherein the membrane is partially or completely enclosed by a shell, and wherein the shell is coiled such that the maximum linear dimension of the coiled shell is no greater than one tenth of the maximum linear dimension of the shell in an uncoiled configuration.

In the present specification, when tubular membrane is referred to in the singular this term may also encompass a plurality of tubular membranes. Each reference to a singular tubular membrane or preferred feature thereof includes one or some or all of the plurality of tubular membranes encompassed by the term.

With regard to module shell length, prior art teaches that for systems where mass transfer on the shell side of the module is an important consideration in the efficiency of the membrane process, shorter shells are preferable. Thus a person skilled in the art has been taught to minimise the length of shell. For example, Prasad and Sirkar AIChE Journal 1988 34 p177 teach that the shell side mass transfer

coefficient is proportional to the inverse one third power of the shell length.

In contrast, we have found that the length of the shell, all other things being equal, has little or no effect on the mass transfer coefficient. Furthermore, for any given area of membrane relative to the shell volume, and any given flowrate of fluid on the shell side of the membrane module (i.e. the volume internal to the shell but external to the tubular elastomeric membranes), a longer shell provides a smaller cross sectional area for flow of the shellside fluid. The velocity in the shell side will be greater than for a module which has the same membrane area per shell volume and the same shellside flowrate, but which is shorter in length. Thus it is clear to those skilled in the art that the rate of mass transfer will be higher in the longer module. Hence the present invention is advantageous.

Flow distribution problems are common on the shell side of shell and tube membrane module designs. Costello et al. Journal of Membrane Science 1993 80 p9 , Noda et al . Journal of Membrane Science 1979 5 p209, and Siebert et al. Sep.Sci.Tech. 28 p343 describe how problems with poor flow distribution on the shell side of modules reduce mass transfer coefficients in hollow fibre bundles. The present invention is further advantageous because modules which for any given area of membrane relative to the shell volume, and any given flowrate of fluid on the shell side of the membrane module, have longer shells, the pressure drop per length of shell will be higher. This increased pressure drop per length may tend to provide more uniform distribution of flow across the shell side cross section of the module.

These advantages may be particularly apparent for those processes whose objective is the transfer of selective species which make up less than 1% by weight of either the first fluid or the second fluid across a membrane from one fluid to another. Also these advantages may be apparent in processes whose objective is the transfer of selective species which make up less than 1% by weight of either the first fluid or the second fluid across a membrane from one fluid to another system and in which mass transfer on the shell side of the module is an important consideration in the efficiency of the membrane process.

Thus, in a preferred aspect the substance is present in either the first fluid or in the second fluid in amount of no greater than 2 wt.%, more preferably in amount of no greater than 1 wt.%, more preferably in amount of no greater than 0.5 wt.%.

The present inventors also appreciate that increasing shell length and membrane tube length, leads to a higher pressure drop per tube at equal flow of fluid within the tube. This higher pressure drop, provided by longer tubes, will make the distribution of the total flow of fluid within the tube across the plurality more even.

With regard to the length of membrane module shells, commercially available shell and tube style modules generally use shells of less than 5 metres maximum linear dimension. This is due to the difficulties in locating modules over 5 metres on industrial sites, since a 5 metre length rigid shell requires either a 5 metre horizontal space for installation, or a support capable of maintaining it vertically, which prejudices production of shells over this length.

With regard to another preferred embodiment of the present invention, it is to be understood that commercially available modules utilising hollow fibres use rigid materials for the shell of the module, and are typically not more than 5 metres in length. As discussed above, the prior art teaches that the mass transfer on the shell side of the module will be reduced in proportion to the length of the shell. Thus a person skilled in the art has been taught to minimise the length of shell.

In contrast, we have found that the length of the shell, all other things being equal, has little or no effect on the mass transfer coefficient. This finding is in accordance with the teachings of Costello et al. Journal of Membrane Science 1993 80 p9.

In accordance with the present invention we have also appreciated that increasing shell length, and therefore increasing membrane tube length, leads to a higher pressure drop per tube at equal flow of fluid within the tube. This higher pressure drop, provided by the longer tubes, will make the distribution of the total flow of

fluid within the tube across the plurality of tubes more even. This is advantageous.

Thus, in a further preferred embodiment of the present invention there is provided a method as described above wherein the membrane tubes are contained within a flexible shell having a length of greater than 5 metres.

In yet a further aspect of the present invention there is provided a flexible shell having a length of greater than 5 metres containing a plurality of elastomeric membrane tubes.

Preferably, the elastomeric membrane is a non porous membrane.

The elastomeric membrane may be formed from any suitable elastomer or elastomers. Preferably, the elastomer is selected from polydimethylsiloxane (PDMS) and other modified polysiloxanes, ethylene-propylene diene (EPDM), polyolefin elastomers, polynorbornene, polyoctenamer, polyurethane, butadiene and nitrile butadiene rubber, natural rubber, butyl rubber, polychloroprene (Neoprene), epichlorohydrin, polyacrylate, elastomers based thereon, derivatives thereof, mixtures thereof and composites thereof.

An external surface of the membrane may be braided with a support material such as by way of non-limiting example mesh comprising metal wire, polymer strands, or natural or synthetic cotton. Braiding will increase the internal pressure which can be applied inside the membrane tube. This may be particularly important when long membranes are used in the coiled shell of the present invention in which the pressure drop created by the fluid passing down the tube may be greater than the burst pressure of the unbraided elastomer tube.

Preferably, the substance to be transferred from the first fluid is selected from any one or more of: a heavy metal, a concentrated acid stream, a concentrated alkali stream, or an aqueous medium which contains at least one organic material.

Preferably, the first fluid and/or the second fluid contains a chemical oxidising agent, for example hydrogen peroxide or ozone, with or without catalysts such as the well known Fentons reagent, or titanium dioxide combined with UV light, chemical reducing reagents, for example palladised iron in an anoxic environment or a microbiological material.

Preferably, the microbiological material is selected from catalytically active biological material, in particular whole cells (viable or non-viable), cell fragments, enzymes, or any combinations thereof .

When the first fluid and/or the second fluid contains microbiological material, the or each microbiological containing fluid may also contain an oxygen containing gas. Preferably, the oxygen containing gas is air.

Preferably, the first fluid is selected from water; aqueous solutions containing organic material(s) and/or inorganic material(s); gases; organic liquids for example hexane, hexadecane, decanol, toluene, benzene, dichloromethane, dimethylsulfoxide, dimethylformamide, tetrahydrofuran, silicone oil, hydrocarbon oil; mineral acids; alkalis, derivative and mixtures thereof.

Preferably, the first fluid is an aqueous medium.

Preferably, the second fluid is selected from water; aqueous solutions containing organic material(s) and/or inorganic material(s); gases; organic liquids for example hexane, hexadecane, decanol, toluene, benzene, dichloromethane, dimethylsulfoxide, dimethylformamide, tetrahydrofuran, silicone oil, hydrocarbon oil; mineral acids; alkalis, derivative and mixtures thereof.

Preferably, the second fluid is an aqueous medium.

The velocities of the fluids will be dependent on a number of factors including the cross-sectional area for flow.

Preferably, the relative velocity of the first and second fluids is in the range 0.005 to 500 ms^{-1}.

Preferably, the velocity of the first fluid is in the range 0.01 to 5 ms^{-1}. More preferably, the velocity of the first fluid is in the range 0.05 to 2 ms^{-1}.

Preferably, the velocity of the second fluid is in the range 0.01 to 5 ms^{-1}. More preferably, the velocity of the second fluid is in the range 0.05 to 2 ms^{-1}.

Preferably, the transmembrane pressure differential is in the range -2.0 to 5.0 bar. More preferably, the transmembrane pressure differential is in the range -1.0 to 3.0 bar.

By the term "transmembrane pressure differential" we mean the difference between the pressure exerted on each of the two sides of a membrane at any given point on the membrane. For example, in a tubular membrane the transmembrane pressure differential is the difference between the pressure exerted on the internal and external walls of the tube at any given point along the length of the membrane tube.

Preferably, the tubular membrane is of circular cross-section.

Preferably, the tubular membrane is from 5 to 200, more preferably 5 to 100 metres in length. More preferably, the tubular membrane is from 10 to 50 metres in length.

Preferably, the tubular membrane has an inner diameter of at least 0.5 mm. More preferably, the tubular membrane has an inner diameter of from 0.5 to 10.0 mm.

Preferably the tubular membrane has a length to diameter ratio of greater than 1,000. More preferably the tubular membrane has a length to diameter ratio of from 2,000 to 100,000. Yet more preferably the tubular membrane has a length to diameter ratio of from 2,000 to 20,000.

In the aspect of the present invention wherein a plurality of tubular membranes are provided, the tubular membranes are preferably packed into a shell at a packing fraction 0.2 to 0.8. More preferably, the tubular membranes are packed into a shell at a packing fraction 0.4 to 0.6.

The "packing fraction" is defined by the following equation

$$\text{Packing fraction} = \frac{\text{volume of shell occupied by tubes}}{\text{volume of shell}}$$

In a preferred embodiment a tube having a length to diameter ratio of greater than 3000 and having an inner diameter of at least 0.5 mm is used to prepare a system of modules for subsequent operation. In this embodiment, the module requires a low amount of potting per length of tube, and therefore can be constructed more economically. Here, "potting" refers to the method which is used seal the membrane tubes into the shell, and is generally known to those skilled in the art of module manufacture.

In a preferred embodiment the tubular membrane may be looped one or more times within the shell. The looped tubular membrane(s) may run substantially parallel to itself and/or each other and/or to the axis of the shell. In this embodiment each looped tube runs a number of times through the shell or a portion thereof. Thus the path length of the tubular membrane through the shell is increased and, if a plurality of membranes are provided, the number of tubular membranes in a shell may be reduced. This is advantageous because the amount of potting per length of tubular membrane may be reduced. For example, a shell, such as a shell of 50 NB, may contain up to 50 passes of a tubular membrane having an internal diameter of 3 mm and operate effectively. The shell may contain 5 to 10 tubular membranes looped in this manner and therefore only 5 to 10 will have to be potted into or otherwise connected to the endpieces of the shell.

In a further preferred embodiment the tubular membrane may be coiled within the shell. The coiled tubular membrane may be substantially perpendicular to the axis of the shell. In this embodiment by increasing the path length of the tubular membrane through the shell, the number of tubular membrane in a shell may be reduced. This is advantageous because the amount of potting per length of tubular membrane may also be reduced.

Installation of systems comprising membrane tubes having the preferred features described above is also more economical than systems of the prior art because fewer module-to-pipework connections are needed per length of tube.

Installation of systems comprising membrane tubes having the preferred features described above also confer the advantage of a more even distribution of flow of the fluid within the plurality of tubes in the bundle through a higher pressure drop per tube.

The material from which the shell is formed is preferably selected from polyethylene, polyvinylchloride, polypropylene, or composites made from combinations of metals and plastics.

Preferably, the composite comprises a helically wound metal or metal mesh supporting polymer layers. Preferably, the metal is stainless steel mesh. Preferably, the polymer is a PTFE liner.

Containers comprising composite materials made from combinations of metals and plastics confer the advantage that they may be readily rolled into a compact shape, for example a helix or spiral. Such shapes allow ease of handling and installation while simultaneously allowing for the use inside the container of long membrane tubes i.e. tubes having a length to diameter ratio greater than 1000, with an internal diameter at least 0.5 mm.

Preferably the shell is constructed from a material which is sufficiently flexible that it can be coiled, preferably in a helical or spiral configuration, whose maximum linear dimension is less than one tenth of the full extended length of the shell.

Preferably the shell is constructed from a flexible material which is circular in cross section and for which the ratio of the fully extended length of the shell relative to its internal diameter is greater than 100, even more preferably greater than 200.

The shell may be constructed from a material which is sufficiently flexible that it can be coiled into a helix with a radius of preferably less than 50 times, more preferably 40 times, yet more preferably 30 times, the internal diameter of the shell.

There are various problems encountered in the commercial scale use of tubular elastomeric membranes for contacting two fluid streams for the purposes of allowing specific chemical species to selectively permeate across a membrane from one stream to another. Elastomeric tubes can possess a relatively low intrinsic strength and rigidity, and so may collapse inwards if subjected to modest transmembrane pressure differentials - such as when the external pressure is slightly greater than the internal pressure. If subjected to an internal pressure which is slightly greater than the external pressure, the tubes may rupture.

For example, silicone rubber tubes with an internal diameter (i.d.) of 3 mm and wall thickness of 0.3 mm may collapse inwards when the external pressure is 0.5 bar greater than the internal pressure i.e. under a transmembrane pressure differential of 0.5 bar greater pressure at the external surface of tube. Moreover, such tubes can rupture when the internal pressure is less than 2.0 bar greater than the external pressure i.e. under a transmembrane pressure differential of less than 2.0 bar greater pressure inside the tube.

Counter-current operation is not always desirable, For example, counter-current flow is not desirable when porous membranes are utilised to contact two immiscible phases, as in EP-A-0120285. In such systems it is important that the transmembrane

pressure differential does not exceed the breakthrough pressure of the pores. If the breakthrough pressure is exceeded, then a (i.e. the first) phase which is under higher pressure may breakthrough the membrane and enter another (i.e. a second) phase. The second phase will be contaminated with the first phase and, in the case of the two phases being aqueous and hydrophobic respectively, an emulsion will be formed.

Thus, although the use of counter-current flow is advantageous for many systems, co-current flow is generally used for contacting two fluids in systems containing a porous membrane. The problem of pore breakthrough of course does not apply to non-porous membranes.

By the term "co-current" we mean two fluids are flowing in substantially the same direction.

In systems requiring flow of fluid on one or both sides of a membrane, flow is often induced by applying pressure to the fluid in which flow is required. In such systems, transmembrane pressure differential may result from the difference between the pressure applied to fluids on different sides of the membrane.

The prior art teaches three principle configurations for using tubular membranes for contacting two fluids between which transfer of chemical species can take place. These configurations are (i) a counter-current manner, for example see US-A-4988443 (see Figure 1 thereof); (ii) a cross-flow configuration, for example see Yang and Cussler AIChE Journal, 1986 32 p 1910 (see Figure 1); and (iii) a co-current configuration, for example EP-A-0120285 (see Figure 1).

It is known, such as from the prior art discussed above, that in many systems use of a counter-current operation is desirable because it maximises the concentration gradient between the two streams. In other words, the concentration driving force for transfer of chemical species is maximised.

Thus in a preferred aspect the method of the present invention comprises the step of passing the first fluid and the second fluid in a co-current manner with respect to each other.

In a further preferred aspect of the method of the present invention, the flow of each of the first fluid and the second fluid is maintained at a constant level and wherein the pressure differential across the tubular membrane is maintained by change in cross-sectional area of the tubular membrane.

This aspect of the present invention is advantageous in that it provides a system wherein at least two fluid streams flow through a shell packed with elastomeric tubes in such a way that the tubes will not collapse inwards or rupture under the effect of the transmembrane pressure differentials created by the flows.

The use of co-current flow with an elastomeric dense-phase membrane is advantageous over other operating methods (cross-flow, counter-current flow). The elasticity of the elastomer allows it to act as a diaphragm between the two fluids. This aspect allows the transmembrane pressure differential to be self regulating.

Self regulation is achieved even in conditions where the membrane becomes heavily coated with material which increases the axial pressure drop on one side. When the flows of two fluids are fixed, for example by the use of appropriate pumps, if one of the surfaces of the membrane becomes coated with material, for example biological material, this will tend to increase the axial pressure drop of the fluid flowing on the side of the membrane which is being coated.

The self regulating nature of the present invention will be illustrated by the following scenarios.

Scenario 1 (External Growth): if biological growth occurs on the outside of a membrane tube, the cross-section for flow of the fluid outside the tubes (the external fluid) will decrease. This will result in an increase in the axial pressure drop of the

external fluid along the length of the membrane. This axial pressure drop increase will be transmitted inwards through a tendency to make the tubes partially collapse. The partial collapse of the tubes will in turn reduce the flow area for fluid within the tubes (the internal fluid), and so cause an increase in the axial pressure drop of the internal fluid along the length of the membrane. The net effect of the two axial pressure drop increases will be that the axial transmembrane pressure differential will not be significantly altered from its original profile.

Scenario 2 (Internal Growth): if biological growth occurs on the inside of a membrane tube, the cross-section for flow of the fluid inside the tubes (the internal fluid) will decrease. This will result in an increase in the axial pressure drop of the internal fluid along the length of the membrane. This axial pressure drop increase will be transmitted outwards through a tendency to make the tubes expand. The expansion of the tubes will in turn reduce the flow area for fluid outside the tubes (the external fluid), and so cause an increase in the axial pressure drop of the external fluid along the length of the membrane. Once again, the net effect of the two axial pressure increases will be that the axial transmembrane pressure differential will not be significantly altered from its original profile.

The self regulatory pressure effect of the present invention is a preferred feature for elastomeric membrane tubes which have a lower intrinsic strength and rigidity than porous hollow fibres, and so would otherwise be more susceptible to collapse or rupture.

The use of a coiled shell with long membrane tubes leads to higher axial pressure drops down both the shell and tube sides of the shell than would occur for shorter tubes. The pressure balancing diaphragm effect produced by co-current flow becomes an even greater advantage when the axial pressure drops are high and so is a greater advantage with the coiled shell of the present invention.

With regard to a further preferred aspect of the present invention, the applicant has recognised that when two or more elastomer tubes are packed in a coiled shell, they

tend to bunch together at the inside radius of the shell. Furthermore, elastomer tubes, for example silicone rubber tubes, tend to bunch together when surrounded with aqueous solution due to their hydrophobicity. All of these factors exacerbate the poor distribution of flow outside of the tubes which is known from the prior art to reduce mass transfer performance.

A further problem of closely packed tubes which is also acknowledged by the prior art is that irregularities in the flow pattern in a shell packed with hollow fibres may adversely affect mass transfer. Costello et al. Journal of Membrane Science 1993 80 p9 describe how at high packing densities of fibres in a shell, the fibres are close together and may even touch, leading to dead zones where mass transfer is poor. Other reports also describe how problems with poor flow distribution reduce mass transfer coefficients in hollow fibre bundles (Noda et al . Journal of Membrane Science 1979 5 p209, Siebert et al. Sep.Sci.Tech. 28 p343).

GB-A-2188563, EP-A-0461789, and EP-A-0186293 disclose polymeric membranes with external surfaces containing protrusions which run longitudinally down the membrane, and where the protrusions are formed as an integral part of the membrane material during moulding. EP-A-0186293 claims these protrusions hold membranes apart when the membranes are packed in a cylindrical shell.

In a preferred embodiment of the present invention there is provided a method as defined above wherein the tubular membrane has protrusions extending from the external surface thereof.

The use of a coiled shell packed with elastomeric membrane tubes produces a tendency for the elastomeric membrane tubes to bunch at the wall of the shell which faces the centre of the coil. In addition, the provision of protrusions counters this tendency and so increases the advantage of using protrusions.

Use of a plurality of tubular membranes comprising protrusions in accordance with the present invention avoids the bunching together of the tubes, or the tube walls

touching and reducing the flow or mass transfer local to the tube. The protrusions which are provided hold the tubes apart, at preferably a predetermined distance.

The present invention also encompasses a method and an apparatus comprising combinations of one or more tubular membranes according to the present invention comprising protrusions and one or more tubular membranes according to the present invention which do not include protrusions.

The protrusions may be produced at the time of extrusion of the elastomer tube, or affixed at some point after the tube is produced.

The protrusions may take any form which produces the desired effect. The protrusions may take the form of ridges protruding radially out from the tube walls. These types of protrusions confer the advantage of providing clear flow channels through the fibre bundle even when the tubes are packed at their maximum density in the shell. Such protrusions achieve this effect even when multiple tubes are packed at random into a shell.

The protrusions may be continuous or discontinuous along the length of the tubular membrane. Preferably, the protrusions are continuous along the length of the tubular membrane.

In a preferred embodiment at least two tubes are joined side by side (in parallel). Preferably, the tubes are joined to each other by at least one of their protrusions.

Thus, the invention provides an effective means for contacting two fluids by passing them across surfaces of a tubular elastomeric membrane. The invention may be utilised for any process in which the desired chemical species permeate across the elastomeric membrane.

The invention will now be described, by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a cross-section of a shell, in accordance with the present invention, packed with tubes provided with protrusions.

Figure 2 is a cross-section of a membrane tube with protrusions in accordance with the present invention.

Figure 3 is a coiled shell containing elastomer tubes in accordance with the present invention.

Figure 1 illustrates a preferred exchange system for use in accordance with the present invention. The exchange system comprises tubular membranes (2) with protrusions (3).

The membranes are packed into a shell (1) and a first fluid (4) is passed through the shell (1). A second fluid (5) is passed through the membrane tubes (2). The first fluid (4) and the second fluid (5) are passed in a direction co-current with respect to each other.

Figure 2 shows a cross-section of a membrane tube (2) used in the exchange system of Figure 1. The tube is formed from an elastomeric membrane and has a circular cross-section. Four continuous protrusions (3) running the length of the tube are provided. These equally are spaced on the circumference of the tube (2).

Figure 3 shows an exchange system in accordance with a preferred embodiment of the present invention. A flexible shell (11) is provided which is coiled into a helix. Within the shell a plurality of elastomeric membrane tubes (2) are provided. The membrane tubes are packed as described above using potting (6).

A first fluid (5) is passed through the elastomeric membrane tubes (2). A second fluid (4) is passed through the shell (1). The fluids flow co-currently with respect to each other.

The operation of the system according to the present invention will now be described, with particular reference to Figure 3..

Example 1

An aqueous process stream (5) containing organic compounds was passed through a plurality of elastomeric membrane tubes (2). A second aqueous stream (4) containing micro-organisms and nutrients, was passed through a flexible shell (11). The organic compounds present in the process stream (5) diffused across the membrane tubes (2) and were consumed by the micro-organisms in the micro-organism containing stream (4), thus maintaining the driving force for the mass transfer.

Example 2

An aqueous process stream (5) containing heavy metals was passed through a plurality of elastomeric membrane tubes (2). A second aqueous stream (4) containing a hydrogen sulphide producing micro-organism was passed through a flexible shell (11). The hydrogen sulphide passed through the membrane (2) and precipitated the heavy metals as metal sulphides. These were then collected from the process stream (5) by sedimentation after it passed out of the flexible shell (11).

In a modification of this embodiment, the micro-organism was replaced by a chemical means for producing hydrogen sulphide, a combination of reagents sodium sulphite and hydrochloric acid.

Example 3

An organic stream (4) containing a biotransformation substrate was passed through a flexible shell (11). An aqueous stream (5) containing catalytically active biological material was passed through a plurality of elastomeric membrane tubes (2). The biotransformation substrate passed through the membrane (2) and was converted to product in a biologically catalysed reaction. The product diffused back across the membrane (2) and exited the module in the organic stream (4).

Example 4

An aqueous process stream (5) containing organic compounds was passed through a plurality of elastomeric membrane tubes (2). A second aqueous stream (4) containing chemical oxidising agents was passed through a flexible shell (11). The organic compounds present in the process stream (5) diffused across the elastomeric membrane (2) and were oxidised by chemical oxidation reactions, thus maintaining the driving force for the mass transfer.

Example 5

An aqueous process stream (4) containing organic compounds was passed through a flexible shell (11). A stream of air (5) was passed through a plurality of elastomeric membrane tubes (2). The organic compounds present in the process stream (4) diffused across the membrane (2) and entered the air stream (5). The air stream flowed out of the shell to an appropriate treatment system for treating organic contaminated gas, for example a bioscrubber, biofilter, chemical oxidation filter or scrubber.

All publications mentioned in the above specification are herein incorporated by reference. Various modifications and variations of the described methods and system of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments. Indeed, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

CLAIMS

1. An apparatus comprising an elastomeric tubular membrane and a shell, wherein the membrane is partially or completely enclosed by a shell, and wherein the shell is coiled such that the maximum linear dimension of the coiled shell is no greater than one tenth of the maximum linear dimension of the shell in an uncoiled configuration.

2. Apparatus according to claim 1 further comprising a first fluid and a second fluid, wherein either the first fluid or the second fluid is held within the internal volume of the membrane and the other of the first fluid or the second fluid is in contact with the external surface of the membrane;

3. A method of transferring at least one substance across a membrane from a first fluid to a second fluid, wherein transfer of the substance from the first fluid to the second fluid occurs across the membrane; wherein the membrane is an elastomeric tubular membrane; wherein either the first fluid or the second fluid is held within the internal volume of the membrane and wherein the other of the first fluid or the second fluid is in contact with the external surface of the membrane;
wherein the membrane is partially or completely enclosed by a shell, and wherein the shell is coiled such that the maximum linear dimension of the coiled shell is no greater than one tenth of the maximum linear dimension of the shell in an uncoiled configuration.

4. An apparatus or method according to any one of claims 1 to 3 wherein the tubular membrane is provided with protrusions extending from the external surface thereof.

5. An apparatus or method according to claim 4 wherein the protrusions are continuous along the length of the tubular membrane.

6. An apparatus or method according to claim any one of claims 1 to 5 wherein the

shell is coiled into a helix with a radius of less than 50 times the internal diameter of the shell.

7. An apparatus or method according to any one of the preceding claims wherein the shell has a length in an uncoiled configuration of greater than 5 metres.

8. An apparatus or method according to any one of the preceding claims wherein the axis of the tubular membrane is parallel to the axis of shell.

9. An apparatus or method according to claim 8 wherein the tubular membrane is looped within the shell.

10. An apparatus or method according to any one of the preceding claims wherein the shell is coiled in a helical or spiral configuration.

11. An apparatus or method according to any one of claims 2 to 10 wherein either the first fluid or the second fluid is liquid and wherein the other fluid is gaseous.

12. An apparatus or method according to any one of claims 2 to 10 wherein the first fluid and the second fluid are liquids.

13. A method according to any one of claims 3 to 12 wherein the method comprises the step of passing the first fluid and the second fluid in a co-current manner with respect to each other.

14. A method according to claim 13 wherein the flow of each of the first fluid and the second fluid is maintained at a constant level and wherein the pressure differential across the tubular membrane is maintained by change in cross-sectional area of the tubular membrane.

15. An apparatus according to claim 1 as substantially described herein and with reference to any one of Figures 1-3.

16. A method according to claim 3 as substantially described herein and with reference to any one of Figures 1-3.

AMENDMENTS TO THE CLAIMS HAVE BEEN FILED AS FOLLOWS

1. An apparatus comprising an elastomeric tubular membrane and a shell, wherein the membrane is partially or completely enclosed by the shell, and wherein the shell is coiled such that the maximum linear dimension of the coiled shell is no greater than one tenth of the maximum linear dimension of the shell in an uncoiled configuration.

2. Apparatus according to claim 1 further comprising a first fluid and a second fluid, wherein either the first fluid or the second fluid is held within the internal volume of the membrane and the other of the first fluid or the second fluid is in contact with the external surface of the membrane;

3. A method of transferring at least one substance across a membrane from a first fluid to a second fluid, wherein transfer of the substance from the first fluid to the second fluid occurs across the membrane; wherein the membrane is an elastomeric tubular membrane; wherein either the first fluid or the second fluid is held within the internal volume of the membrane and wherein the other of the first fluid or the second fluid is in contact with the external surface of the membrane;
wherein the membrane is partially or completely enclosed by a shell, and wherein the shell is coiled such that the maximum linear dimension of the coiled shell is no greater than one tenth of the maximum linear dimension of the shell in an uncoiled configuration.

4. An apparatus or method according to any one of claims 1 to 3 wherein the tubular membrane is provided with protrusions extending from the external surface thereof.

5. An apparatus or method according to claim 4 wherein the protrusions are continuous along the length of the tubular membrane.

6. An apparatus or method according to claim any one of claims 1 to 5 wherein the

shell is coiled into a helix with a radius of less than 50 times the internal diameter of the shell.

7. An apparatus or method according to any one of the preceding claims wherein the shell has a length in an uncoiled configuration of greater than 5 metres.

8. An apparatus or method according to any one of the preceding claims wherein the axis of the tubular membrane is parallel to the axis of shell.

9. An apparatus or method according to claim 8 wherein the tubular membrane is looped within the shell.

10. An apparatus or method according to any one of the preceding claims wherein the shell is coiled in a helical or spiral configuration.

11. An apparatus or method according to any one of claims 2 to 10 wherein either the first fluid or the second fluid is liquid and wherein the other fluid is gaseous.

12. An apparatus or method according to any one of claims 2 to 10 wherein the first fluid and the second fluid are liquids.

13. A method according to any one of claims 3 to 12 wherein the method comprises the step of passing the first fluid and the second fluid in a co-current manner with respect to each other.

14. A method according to claim 13 wherein the flow of each of the first fluid and the second fluid is maintained at a constant level and wherein the pressure differential across the tubular membrane is maintained by change in cross-sectional area of the tubular membrane.

15. An apparatus according to claim 1 as substantially described herein and with reference to any one of Figures 1-3.

16. A method according to claim 3 as substantially described herein and with reference to any one of Figures 1-3.

Application No:	GB 9823963.5	**Examiner:**	R E Hardy
Claims searched:	ALL	**Date of search:**	23 November 1998

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): B1X

Int Cl (Ed.6): B01D (61/00 61/14 61/18 61/24 61/28 63/00 63/06)

Other: Online : WPI,EDOC,JAPIO

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB2036595 A UKAEA : See the Figures	1,3
A	GB1510486 A RHONE-POULENC : See the Figures	1,3
A	GB1362742 A PHILCO-FORD : See the Figures	1,3
A	US5639365 A McLOUGHLIN : See the Figures	1,3
A	WO97/05946 A1 RENSSELAER : See Figure 4	1,3

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